

# PATENT SPECIFICATION

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DRAWINGS ATTACHED

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 (72) Inventor HERBERT LEONARD GEE

(19)



## (54) PROCESS FOR THE PRODUCTION OF ORGANIC ISOCYANATES

- (71) We, QUIMCO G.m.b.H., of 74 Hegibachstrasse, Zürich, Switzerland, a Joint-Stock Company organised under the laws of Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- The present invention is concerned with a continuous method for the production of organic isocyanates by phosgenating organic amines.
- According to known methods, a solution of an amine is reacted with a solution of phosgene in an organic solvent for the preparation of the corresponding isocyanates. It is known to carry out this process at temperatures of up to 240°C. under pressures of up to 7 atmospheres. It is also known to react the amine solution with phosgene in two stages, the first stage resulting in the formation of the carbamoyl chloride by limiting the temperature to below about 130°C. and, in the second stage, the carbamoyl chloride is decomposed at a higher temperature. In these known processes, it is usual to use a large excess of phosgene over amine and in the two step process also in the second high temperature stage.
- A disadvantage of these known processes is the long time required for the overall reaction to be completed. Another disadvantage of known processes, arising from this long reaction time and the need for a large excess of phosgene, is the large amount of phosgene and phosgene-containing reaction mixture required in relation to the amine feed rate. This results in a need for large and costly plants made from corrosion-resistant materials and also in increased toxic hazards in the event of leakage.
- The above problems are increased when producing isocyanates from less reactive amines, particularly aliphatic and cycloaliphatic amines, the corresponding isocyanates of which are of increasing commercial importance.
- It is well known that isocyanates tend to polymerise and decarboxylate at elevated temperatures and we have found that, as the reaction temperature is raised, the reaction completion time decreases faster than the rate of increase of the polymerisation reaction. These reactions are also suppressed by excess phosgene, as are such wasteful side reactions as deamination of the amine hydrochloride produced along with carbamoyl chloride in the first stage of the reaction of the phosgene with the amine. The excess phosgene also decomposes ureas and biurets which result from the reaction of the starting amine with the isocyanate product.
- By effecting the phosgenation reaction at a temperature above the reversible splitting temperature of the urea linkage, i.e. in the range of 150—180°C., for most simple aromatic polyureas, but below the irreversible deamination temperature of aromatic amines and the irreversible decarboxylation of isocyanates to carbodiimides, i.e. above 180°C., a high yield of isocyanate results with only slight excess phosgene requirement. However, to ensure a uniform dispersion of the heat of reaction, it is the practice of the prior art to employ solvents which are liquid and inert to the reactants. These solvents will not dissolve the polyureas formed as intermediates and a heterogeneous system results, long reaction times or high temperatures being required for complete conversion to isocyanate.
- It is an object of the present invention to dispense with the need for a non-participating inert solvent and the mechanical complexity associated with its recovery and recycling.
- It is a further object of the present invention to carry out the reaction in two distinct stages and to include the recycling of part of the isocyanate formed as a reactive solvent. In this way, the excess isocyanate reacts with the hydrogen chloride formed in the first step in an endothermic reaction, thereby reducing the overall amount of heat formed in the first stage of the reaction.
- We have also found that the isocyanate product is an excellent solvent for the various reaction intermediates and that a good heat

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transfer occurs with a low risk of local overheating. By effecting the reaction at an arbitrary pressure above that required to maintain a single phase reaction system, the pressure dependence of specific heat and reaction exothermy result in a reduced temperature rise and we have found it practicable to carry out the reaction adiabatically. The product of the first reaction stage is the carbonyl chloride dissolved in excess isocyanate containing a slight excess of phosgene.

Stage 2 is carried out simultaneously and separately under independent conditions and comprises the thermal pyrolysis of the carbamoyl chloride dissolved in the isocyanate product. By feeding the uncooled mixture from stage 1 into a heated vessel and lowering the pressure by venting off dissolved phosgene and hydrogen chloride gas formed as co-product in the pyrolysis of the carbamoyl chloride, there is obtained a non-volatile residue of isocyanate product dissolved in recycle isocyanate. This may be worked up in any conventional way, as may the gaseous phase mixture of phosgene and hydrogen chloride. Because of the wide difference in the boiling points of hydrogen chloride, phosgene and the vast majority of the mono- and poly isocyanates, only simple recovery and purification equipment is required.

Thus, according to the present invention, there is provided a process for the production of organic isocyanates from an amine or amine mixture and phosgene, wherein the amine, preheated to a temperature below its decomposition temperature at superatmospheric pressure, is first reacted with preheated phosgene in the presence of an excess of an organic isocyanate at temperatures and pressures such that the reaction proceeds in a homogeneous liquid phase to give substantially organic carbamoyl chloride(s) dissolved in liquid excess phosgene and excess starting organic isocyanate and then, in a second stage, these organic carbamoyl chlorides are thermally decomposed at a lower pressure to give the isocyanate corresponding to the starting amine mixed with the added excess starting isocyanate.

The organic isocyanate used is preferably a mono-isocyanate and the amine used can be, for example, a reaction product of an aldehyde or ketone and of an organic primary aromatic monoamine, or can be obtained by nitration and subsequent reduction of an aromatic hydrocarbon. The amine used preferably contains no functional groups other than amino groups capable of reacting with phosgene and is preferably a primary amine of a polyamine.

Because of the prevailing high temperature for both reaction steps, the overall reaction time is very short, being in the order of 5 to 60 seconds. This permits the use of pipe

reactors of small volume made from corrosion resistant materials, the resultant cost and hazard reduction largely compensating for the higher cost of high pressure pumps and control equipment.

In a preferred embodiment of the present invention, excess phosgene and co-product hydrogen chloride are separated at a pressure above atmospheric pressure to permit the use of condenser cooling water at ambient temperature and to facilitate the use of a compact plant in relation to output.

In a preferred embodiment of the present invention now to be described, the second reaction stage is effected at an intermediate pressure rather than at the final system pressure, in order to provide greater flexibility in varying the phosgene concentration in the second step. However, this is not an essential requirement of the present invention.

In the preferred embodiment of the present invention now to be described, the first stage of the reaction is carried out adiabatically with all the reactants fed in at temperatures in the range of 120 to 180°C. and the reactant exit temperature kept in the range 180—250°C., the applied pressure being kept constant in the range 100 to 300 atmospheres. The residence time of the reactants in the reaction zone should preferably be in the range of 5 to 150 seconds. The second stage of the reaction is carried out isothermally with all the reactants fed in at temperatures in the range of 120 to 250°C. and the applied pressure being kept constant in the range of 3 to 30 atmospheres. The average residence time of the reactants in the second stage reaction zone should preferably be in the range of 3 to 30 minutes, whilst the product isocyanate discharged from the second stage is preferably cooled to a temperature in the range of 50 to 80°C., prior to recycling.

In the preferred embodiment, as indicated in the accompanying drawing, which shows the essential apparatus and the various flows and temperatures, liquid phosgene is fed in as make-up to crude recycled phosgene held in storage tank (1) at a pressure in excess of 3 atmospheres. Amine feed is taken from liquid storage tank (2) maintained at a pressure of 3 atmospheres by nitrogen gas at this pressure. The tank (2) is heated to 80°C. by heating coils in order to keep the amine liquid. Crude recycled product isocyanate is held in tank (3), under a mixture of phosgene and hydrogen chloride, at a pressure of 3 atmospheres and kept at a temperature of 80°C. by cooling/heating coils.

Crude liquid phosgene at 21°C. and 3 atmospheres pressure is fed to phosgene pump (4), where its pressure is raised to 1000 atmospheres, and then passed through pre-heater (5) to static turbulent flow mixer



(6), where it forms a homogeneous solution with recycled product isocyanate drawn from tank (3) at 80°C. and 3 atmospheres pressure and delivered at a pressure of 100 atmospheres by pump (7) through preheater (8), where its temperature is raised to 150°C., prior to entering mixer (6).

The phosgene/isocyanate solution leaving mixer (6) is divided by valve 9, about 2/3 of the flow being diverted into turbulent flow static mixer (10), where it is mixed with molten amine drawn by pump (11) from tank (2) at 3 atmospheres pressure and at 80°C. and its pressure is raised to 100 atmospheres and discharged to amine preheater (12) in which its temperature is raised to 150°C. prior to entry into static mixer (10). The reacting mixture passes from mixer (10) into adjacent reaction pipe (13) in which reaction stage 1 is completed under adiabatic conditions resulting from mixer (10) and reactor pipe (13) being thermally insulated. Reaction products leaving pipe reactor (13) pass isentropically through pressure reducing valve (14), leaving at a pressure of 20 atmospheres, and immediately enter a separate vessel (15), where the temperature falls to about 150°C., following vaporisation of most of the hydrogen chloride and part of the phosgene. These vapours vent from separator (15) to a low pressure vapour line via pressure reducing valve (16). The liquid mixture in separator (15) runs out into reactor vessel (17) maintained at 20 atmospheres pressure via a balance pipe to separator vessel (15) and at a temperature of 220°C., produced by means of a heating jacket.

The remaining 1/3 of the flow of phosgene/isocyanate mixture from valve (9) enters reactor vessel (17) via pressure reducing valve (18), in which its pressure drops isentropically to 20 atmospheres. Flashed off phosgene and hydrogen chloride vapours leave reactor (17) and enter separator (15), to join the vapours produced there, via a balance pipe connecting vessels (15) and (17). The contents of reactor vessel (17) are stirred continuously and continuously overflow into separator (19) via pressure reducing valve (20) after being in vessel (17) for an average time of 1/2 hour, during which time stage 2 of the reaction is completed in the presence of an increased amount of recycled isocyanate and some excess dissolved phosgene. During this residence time, substantially all traces of undissolved polyureas are dissolved and decomposed. The liquid leaving reactor (17) is now essentially all product isocyanate containing some dissolved phosgene and hydrogen chloride. Following isentropic expansion during passage through valve (20), the mixed liquid and vapours are separated in separator (19) and the vapours at a pressure of 3 atmospheres join similar

vapours leaving valve (16), both streams being at a temperature of about 150°C., and the combined vapours enter low temperature pressure distillation column (21) as vapour feed. The hot, liquid product isocyanate leaves the separator (19) at about 150°C. and runs into recycle isocyanate storage tank (3) maintained at 80°C. by means of a water-cooling coil. A portion of the isocyanate in tank (3) equivalent to the amine feed is withdrawn via level control valve (22) to pressure reducing valve (23) and fed to film evaporator (24) operated at a pressure of 1 atmosphere to strip off all traces of volatiles, including traces of dissolved phosgene and hydrogen chloride, to give output product isocyanate delivered at 200°C. to storage tank (25), where it is cooled to 50°C. by means of a cooling coil, prior to withdrawal for use.

Vapours entering the distillation column (21) are separated into hydrogen chloride gas overheads by means of phosgene refluxing between boiler (26) and condenser (27) cooled with water to 21°C. Hydrogen chloride gas remaining undissolved in the liquid phosgene leaves condenser (27) at 21°C. and 3 atmospheres pressure, mixed with some phosgene vapour, and enters pressurised cold traps (28) and (29), where substantially all the residual phosgene is condensed. Vented hydrogen chloride with a dew point of -60°C. at a pressure of 3 atmospheres leaves the cold trap via pressure reducing valve (30) at 1 atmosphere for recovery or use elsewhere. Liquid phosgene containing dissolved hydrogen chloride runs from cold trap collecting vessel and combined phosgene storage tank (1) maintained at 21°C. by a water-cooling coil to the distillation column reboiler loop (26) to be stripped of dissolved hydrogen chloride. Hot, liquid phosgene overflows from the base of the column (21) containing a minimum of dissolved hydrogen chloride via water-cooled heat exchanger (31) to be recycled by phosgene pump (4).

The following Examples are given for the purpose of illustrating the present invention:—

#### EXAMPLE 1

10 kg. of crude recycled 4,4'-diphenylmethane diisocyanate (crude MDI) containing dissolved phosgene and hydrogen chloride is stored at a temperature of 80°C. and 3 atmospheres pressure under a mixed atmosphere of phosgene and hydrogen chloride vapour.

8 kg. of crude recycled liquid phosgene, containing dissolved hydrogen chloride, is stored at a temperature of 21°C. and 3 atmospheres pressure under a mixed atmosphere of phosgene and hydrogen chloride vapour.



1 kg. of 4,4<sup>1</sup> - diaminodiphenylmethane (MDA) is stored in liquid form at a temperature of 80°C. at 3 atmospheres pressure under an inert atmosphere which is free of oxygen.

10 kg. of crude MDI and 8 kg. of crude phosgene are both simultaneously delivered continuously over a period of 1 hour at a constant rate to a turbulent flow static mixing device to form a homogeneous liquid solution which is then passed through a heater in which the temperature is raised to 148—150°C., following which  $\frac{2}{3}$  of the stream is passed into a second turbulent flow static mixing device and a following connected reaction vessel of 100 ml. volume, both being enclosed in an insulating jacket. Simultaneously with this stream of mixed crude phosgene and crude MDI, there is passed through the second turbulent flow static mixing device and reaction vessel  $\frac{1}{3}$  kg. of molten MDA delivered continuously at a constant rate over a period of 1 hour.

The temperature of the following contents of the reaction vessel remains substantially constant at a temperature of 240°C. as a result of the adiabatic release of reaction heat. The pressure in the reaction vessel is maintained constant at 98—100 atmospheres. The reaction products are continuously discharged into a vapour/liquid separator maintained at a constant pressure of 20 atmospheres. The liquid phase is passed continuously into a second reactor vessel of 5 litres capacity, maintained at a temperature of 218—220°C. by external heating. Simultaneously, the remaining  $\frac{1}{3}$  of the stream of preheated mixture of crude MDI and crude phosgene passes continuously into this 5 litre reactor vessel. The reaction products from this second reactor vessel are continuously discharged into a second vapour/liquid separator maintained at a constant pressure of 3 atmospheres and maintained at a temperature of 148—150°C. by external heating. Liquid reaction products are continuously discharged to the crude recycle MDI storage tank.

Approximately 1 kg. of crude MDI is continuously delivered at a constant rate over a period of 1 hour so as to maintain a constant level in the crude MDI storage vessel to a thin film evaporator operating at 3 atmospheres pressure and having a jacket temperature of 218—220°C., to remove phosgene and hydrogen chloride dissolved in the crude MDI.

There was thus obtained a yield of 94% of theory, based on the amount of MDA used. The product had a boiling point of 188°C. at 2 mm.Hg. and a melting point of 37—38°C.

#### EXAMPLE 2

10 kg. of crude recycle phenyl isocyanate

containing dissolved phosgene and hydrogen chloride is stored at a temperature of 80°C. and 3 atmospheres pressure under a mixed atmosphere of phosgene and hydrogen chloride vapour.

1 kg. of aniline is stored at a temperature of 80°C. at 3 atmospheres under an inert atmosphere free of oxygen.

8 kg. of crude recycled phosgene liquid, containing dissolved hydrogen chloride, is stored as described in Example 1.

Following the procedure of Example 1, the phosgene is mixed with the phenyl isocyanate and the resultant solution preheated to 148—150°C. and mixed with the aniline, which has been preheated to 148—150°C., in two reaction steps, keeping the temperatures, pressures and flow division exactly as described in Example 1 over a period of 1 hour.

The reaction gives approximately 1 kg. per hour of phenyl isocyanate, corresponding to a yield of 96% of theory, based on the amount of aniline used. The product had a boiling point of 55—57°C. at 16 mm.Hg.

#### EXAMPLE 3

10 kg. of crude recycled 4,4<sup>1</sup> - dicyclohexylmethane diisocyanate, containing dissolved phosgene and hydrogen chloride, is stored at a temperature of 80°C. and 3 atmospheres pressure, under a mixed atmosphere of phosgene and hydrogen chloride vapours.

1 kg. of 4,4<sup>1</sup> - diaminodicyclohexylmethane is stored at a temperature of 80°C. at 3 atmospheres pressure under an inert atmosphere free of oxygen.

8 kg. of crude recycled phosgene liquid, containing dissolved hydrogen chloride, is stored as described in Example 1.

Following the procedure of Example 1, the phosgene is mixed with the 4,4<sup>1</sup> - dicyclohexylmethane diisocyanate and the resultant solution preheated to 148—150°C. and mixed with the 4,4<sup>1</sup> - diaminodicyclohexylmethane which has, in turn, been preheated to 148—150°C. in two reaction steps, keeping the temperature, pressures and flow division exactly as described in Example 1 over a period of 1 hour.

The reaction gives approximately 1 kg. per hour of 4,4<sup>1</sup> - dicyclohexylmethane diisocyanate, corresponding to a yield of 82% of theory, based on the amount of 4,4<sup>1</sup> - diaminodicyclohexylmethane used. The product had a boiling point of 167—168°C. at 1.5 mm.Hg.

#### EXAMPLE 4

10 kg. of a crude recycled equimolar mixture of phenyl isocyanate and 4,4<sup>1</sup> - diphenylmethane diisocyanate and containing dissolved phosgene and hydrogen chloride, is stored at a temperature of 80°C. and 3 atmospheres pressure, under a mixed atmo-



sphere of phosgene and hydrogen chloride vapours.

1 kg. of an equimolar mixture of aniline and 4,4'-diaminodiphenylmethane is stored at a temperature of 80°C. at 3 atmospheres under an inert atmosphere free of oxygen.

8 kg. of crude recycled phosgene liquid, containing dissolved hydrogen chloride, is stored as described in Example 1.

Following the procedure of Example 1, the phosgene is mixed with the mixture of mono- and diisocyanates and the resultant solution preheated to 148–150°C. and mixed with the mixture of aniline and 4,4'-diaminodiphenylmethane which had, in turn, been preheated to 148–150°C. in two reaction steps, keeping the temperature, pressure and flow division exactly as described in Example 1 over a period of 1 hour.

The reaction gives approximately 1 kg. per hour of a mixture of phenyl isocyanate and 4,4'-diphenylmethane diisocyanate, corresponding to a mixed product yield of 94%, based on the weight of mixed amines used. Vacuum distillation of the reaction product gave 95% of the theoretical yield of phenyl isocyanate (b.p. 55–57°C./16 mm.Hg.) and 93% of the theoretical yield of 4,4'-diphenylmethane diisocyanate (b.p. 187–188°C./2 mm.Hg.; m.p. 37–38°C.).

#### WHAT WE CLAIM IS:—

1. A process for the production of organic isocyanates from an amine or amine mixture and phosgene, wherein the amine, preheated to a temperature below its decomposition temperature at superatmospheric pressure, is first reacted with preheated phosgene in the presence of an excess of an organic isocyanate at temperatures and pressures such that the reaction proceeds in a homogeneous liquid phase to give substantially organic carbamoyl chloride(s) dissolved in liquid excess phosgene and excess starting organic isocyanate and then, in a second stage, these organic carbamoyl chloride(s) are thermally decomposed at a lower pressure to give the isocyanate corresponding to the starting amine mixed with the added excess starting isocyanate.

2. A process according to claim 1, wherein the added organic isocyanate corresponds with the said amine, the product obtained being an increased quantity of the added isocyanate.

3. A process according to claim 1 or 2, wherein the amine used is a primary amine.

4. A process according to claim 1 or 2, wherein the amine used is a polyamine.

5. A process according to any of the preceding claims, wherein the amine used contains no functional groups other than amino groups capable of reacting with phosgene.

6. A process according to any of the preceding claims, wherein the amine used is a reaction product of an aldehyde or ketone and an organic primary aromatic monoamine.

7. A process according to any of claims 1 to 5, wherein the amino used is obtained by nitration and subsequent reduction of an aromatic hydrocarbon.

8. A process according to any of the preceding claims, wherein the organic isocyanate is a monoisocyanate.

9. A process according to any of the preceding claims, wherein the reactants are fed into the first stage at a temperature of 120–180°C., the reaction pressure being kept constant in the range of 100 to 300 atmospheres.

10. A process according to any of the preceding claims, wherein the residence time in the first stage is 5 to 150 seconds.

11. A process according to any of the preceding claims, wherein the reaction in the second stage is carried out isothermally at a constant pressure in the range of 3 to 30 atmospheres, the reactants being fed in at a temperature of 120 to 250°C.

12. A process according to any of the preceding claims, wherein the residence time in the second stage is 3 to 30 minutes.

13. A process according to claim 1 for the production of organic isocyanates, substantially as hereinbefore described and exemplified and with reference to the accompanying drawing.

14. Organic isocyanates, whenever produced by the process according to any of claims 1 to 13.

VENNER, SHIPLEY & CO.,  
Chartered Patent Agents,  
Rugby Chambers,  
2, Rugby Street,  
London, WC1N 3QU.  
Agents for the Applicants.



